

REMARKS/ ARGUMENTS

The Office Action of September 4, 2003 has been carefully reviewed and this response addresses the Examiner's concerns.

Claims 1-3, 6-7, 10-12, 14-19, 66-67, 69-70 and 125 are pending in the application. Claims 22-65 and 119-124 are withdrawn from consideration. Claims 1 and 10 are amended in order to more clearly express the invention. Claims 6, 7, 11, 17, 66, 67, 69, 70 are amended in order to Claim 125 is added.

In view of the examiner's earlier and present restriction requirements, applicants retains the right to present claims 22-65 and 119-124 in divisional applications.

Claims 1-3, 6-7, 10-12, 14-19, 66-67 and 69-70 were rejected under 35 USC 112, first paragraph. Claims 1-3, 6-7, 10-12, 14-19, 66-67 and 69-70 were rejected under 35 USC 112, second paragraph.

Claims 1-2, 10, 12, 14, and 69-70 were rejected under 35 U.S.C. §102(b) as being anticipated by Hutchens et al., U.S. Patent 5,719,060. Claims 1-3, 10, 12, 14, 17, 66 and 69-70 were rejected under 35 U.S.C. §102(e) as being anticipated by Nelson et al. (U.S. Patent 5,955,729). Claims 1-2, 6-7, 10-12, 14, 17, 66 and 69-70 were rejected under 35 U.S.C. §102(e) as being anticipated by Siuzdak et al. (U.S. Patent 6,288,390). Claims 1-2, 6-7, 10-12, 14, 17, 66 and 69-70 were rejected under 35 U.S.C. §103(a) as being unpatentable over Siuzdak et al. (U.S. Patent 6,288,390) in view of Mian et al. (6,319,469). Claims 1 and 15-16 were rejected under 35 U.S.C. §103(a) as being unpatentable over Siuzdak et al. (U.S. Patent 6,288,390) in view of Farmer et al. (J. Mass Spectrom., 1998. 3:697-704).

The amended claim 1, rewritten in order to more clearly express the invention, overcomes the 35 USC 112 rejections.

Support in the Specification to Amendments to Claim 1 and Added dependent Claim 125

The depositing a continuous film having optical properties and species adsorption properties essentially the same as the optical properties and the species adsorption properties of

the continuous film bulk material is supported by p. 14, lines 13-23 ("*The continuous film (no voids) semiconductor material of Table 1 is demonstrated herein using PECVD. These films are distinguished by having no void structure.. As a consequence their optical properties and species adsorption properties are essentially the same as bulk material. That is, silicon films of this morphology have the species adsorption properties, optical reflectance, optical absorption, and analyte adsorption properties of a silicon wafer.*").

Claim 125 finds support in p. 8, lines 24-26 ("*In an embodiment of this invention the material is a continuous semiconductor film having no voids and deposited by PECVD.*") and in p. 18, lines 14-15 ("*The continuous film (no voids) semiconductor material of Table 1 is demonstrated herein using PECVD.*").

Claims 1-2, 10, 12, 14, and 69-70 were rejected under 35 U.S.C. §102(b) as being anticipated by Hutchens et al., U.S. Patent 5,719,060.

Applicants respectfully traverse these rejections for the reasons presented below.

In order to better understand the differences between the present invention and the Hutchens et al. patent it should be recognized that in the Applicants' invention the continuous films have optical properties and species adsorption properties essentially the same as the optical properties and the species adsorption properties of the continuous film bulk material and do not have surface associated molecules to which the sample is chemical attached.

In comparison, the '060 patent (Hutchens) discloses sample presenting means utilizing surface associated molecules to effectuate the chemical attachment of sample to the sample presenting means (col. 13, lines 40- 67, col. 14, lines 1-41). The adsorption to the sample presenting means is accomplished by docking or tethering (Hutchens, col. 14, lines 5-9, "*Such surfaces (i.e., sample presenting means) allow for very strong (i.e., stable, covalent) analyte attachment or adsorption (i.e., docking or tethering) processes that are covalent but reversible upon irradiation (i.e., photolabile.*"; Hutchens, col. 14, lines 36-45, "*The invention herein presents, a sample presenting means (i.e., probe element surface) with surface-associated (or*

surface-bound) molecules to promote the attachment (tethering or anchoring) and subsequent detachment of tethered analyte molecules in a light-dependent manner, wherein the said surface molecule(s) are selected from the group consisting of photoactive (photolabile) molecules that participate in the binding (docking, tethering, or crosslinking) of the analyte molecules to the sample presenting means (by covalent attachment mechanisms or otherwise).")

The discussion below demonstrates that a) Hutchens does not teach the depositing of a continuous film having species adsorption properties essentially the same as the species adsorption properties of the continuous film bulk material and b) that Hutchens does not teach depositing a continuous film that has optical properties essentially the same as the optical properties of the continuous film bulk material.

a) Hutchens does not teach depositing a continuous film that has species adsorption properties essentially the same as the species adsorption properties of the continuous film bulk material.

A bulk material, as used in the Applicants' invention, would not have surface associated molecules. In a preferred embodiment of Hutchens' invention, "[the] sample presenting surface comprises the surface of a probe tip for use in a time-of-flight mass spectrometry analyzer. In addition, the preferred embodiment presents an affinity capture device or photolabile attachment molecule that is chemically bonded to [the] sample presenting surface, physically adhered to [the] sample presenting surface, chemically bonded to said analyte molecules, or is adapted to biologically adhere to said analyte molecules." (Hutchens, col. 17, lines 42 - 51). Assuming *arguendo* that the surface or sample presenting means is a continuous film, species adsorption (docking, tethering, or crosslinking) occurs via the surface associated molecules. As stated above, a bulk material, as used in the Applicants' invention, would not have surface associated molecules in order to produce species adsorption. Therefore, Hutchens does not teach depositing a continuous film that has species adsorption properties essentially the same as the species adsorption properties of the continuous film bulk material.

b) Hutchens does not teach depositing a continuous film that has optical properties essentially the same as the optical properties of the continuous film bulk material.

Hutchens does not discuss optical properties. However, Hutchens discloses "a sample presenting means (i.e., probe element surface) with surface-associated (or surface-bound) molecules" (Hutchens, col. 14, lines 36-38). A sample presenting means with surface associated molecules, as used by Hutchens, is a composite structure and the dielectric constant of a composite material is given by a combination of the two dielectric constants (Bergman theorem or the Clausius-Mosotti equation). Considering *arguendo* that the surface or sample presenting means is a continuous film, the dielectric constant of the composite depends on the combination of the dielectric constant of the continuous film (surface or sample presenting means) bulk material and dielectric constant of the material of the surface associated molecules. The dielectric constant determines several optical properties of interest. Thus, the optical properties of the sample presenting means with surface associated molecules would be different from that of the surface or sample presenting means bulk material. Therefore, Hutchens does not teach depositing a continuous film that has optical properties essentially the same as the optical properties of the continuous film bulk material.

Thus, Hutchens neither discloses depositing a continuous film having optical properties nor discloses depositing a continuous film having species adsorption properties essentially the same as the optical properties and the species adsorption properties of the continuous film bulk material.

To anticipate a claim a reference must teach every element of the claim. (MPEP § 2131). As pointed above, Hutchens does not teach depositing a continuous film having optical properties and species adsorption properties essentially the same as the optical properties and the species adsorption properties of the continuous film bulk material.

Applicants respectfully assert that amended Claim 1 is not anticipated by the '060 patent (Hutchens) and neither are any of the dependent claims. In addition, in view of the specific needs of Hutchens (as discussed above) and since Hutchens is lacking a patentable feature present in claim 1 and the dependent claims of the Applicants' invention, a modification of Hutchens under 35 U.S.C. § 103 would also be inapplicable because such modifications are not taught by nor

obvious under Hutchens, and if incorporated into Hutchens, would render Hutchens inoperable for its intended functions.

Claims 1-3, 10, 12, 14, 17, 66 and 69-70 were rejected under 35 U.S.C. §102(e) as being anticipated by Nelson et al. (U.S. Patent 5,955,729).

Applicants respectfully traverse these rejections for the reasons presented below.

As in Hutchens, Nelson et al (U.S. Patent 5,955,729, hereinafter referred to as Nelson) also disclose utilizing surface associated molecules to effectuate the chemical attachment of a sample to the surface of a sensor chip or metal layer. (col. 3, lines 64-66, col. 8, lines 29-33, col. 7, lines 45-50). As is shown below, a) Nelson does not teach the depositing of a continuous film having species adsorption properties essentially the same as the species adsorption properties of the continuous film bulk material and b) Nelson does not teach depositing a continuous film that has optical properties essentially the same as the optical properties of the continuous film bulk material.

a) Nelson does not teach depositing a continuous film that has species adsorption properties essentially the same as the species adsorption properties of the continuous film bulk material.

In one embodiment of Nelson's invention, the "sensor chip (100) is a transparent material (112) having a metal layer (114) deposited thereon. Interactants (120), which in FIG. 1A are depicted as antibodies, are immobilized on metal layer (114)." (Nelson, col. 7, lines 46-50). "As a sample containing interactant(s) (124) passes through flow channel (122) antibodies (120) selectively bind thereto." (Nelson, col. 7, lines 55-57). Therefore, the adhesion (binding) properties of the metal layer in the sensor chip are not the same as the bulk material of the metal layer since the analyte binds chemically to the antibodies immobilized on the metal layer. In another embodiment of Nelson's invention, "a surface matrix such as a hydrogel of a polysaccharide (e.g., carboxymethylated dextran) may be affixed to the metal layer by a suitable linking layer." (Nelson, col. 8, lines 21-35). Such a surface matrix "can readily immobilize capturing molecules." (Nelson, col. 8, lines 30-31). As described by Nelson (col. 8, lines 21-35) and in PCT International Publication No. WO 90/05303 (referenced by Nelson), the analyte

binds chemically to the capturing molecules immobilized on the surface matrix. Therefore, the adhesion (binding) properties of the surface matrix are not the same as the bulk material of the surface matrix since the analyte binds chemically to the capturing molecules immobilized on the surface matrix. All the above techniques involve modifying the species adsorption properties of the surface matrix or metal layer bulk material. Therefore, Nelson does not teach depositing a continuous film that has species adsorption properties essentially the same as the species adsorption properties of the continuous film bulk material.

b) Nelson does not teach depositing a continuous film that has optical properties essentially the same as the optical properties of the continuous film bulk material.

Nelson utilizes the change in optical properties for detection. *"The detection principle relies on the optical phenomenon of surface plasmon resonance (SPR), which detects changes in the refractive index of the solution close to the surface of a sensor chip."* (Nelson, col. 7, lines 32-44). The initial surface concentration modifies the refractive index from that of the metal layer or the surface matrix since the immobilized interactants can be considered as part of a composite structure (which can be analyzed by the Bergman theorem or the Clasius-Mosotti equation). The refractive index is a function of the dielectric constant. The dielectric constant of a composite material is given by a combination of the two dielectric constants. Considering that the metal layer or the surface matrix as a continuous film, the dielectric constant of the composite depends on the combination of the dielectric constant of the continuous film (the metal layer or the surface matrix) bulk material and dielectric constant of the material of the surface associated molecules. The dielectric constant determines several optical properties of interest. Thus, the optical properties of the metal layer or the surface matrix disclosed by Nelson are different from those of the continuous film (metal layer or surface matrix) bulk material. Therefore, Nelson does not teach or disclose a continuous film that has optical properties essentially the same as the optical properties of the continuous film bulk material.

As stated above, Nelson neither discloses depositing a continuous film having optical properties nor discloses depositing a continuous film having species adsorption properties

essentially the same as the optical properties and the species adsorption properties of the continuous film bulk material.

To anticipate a claim a reference must teach every element of the claim. (MPEP § 2131). Nelson does not teach depositing a continuous film having optical properties and species adsorption properties essentially the same as the optical properties and the species adsorption properties of the continuous film bulk material.

Applicants respectfully assert that amended Claim 1 is not anticipated by the '729 patent (Nelson) and neither are any of the dependent claims. In addition, in view of the specific needs of Nelson (as discussed above) and since Nelson is lacking a patentable feature present in claim 1 and the dependent claims of the Applicants' invention, a modification of Nelson under 35 U.S.C. §103 would also be inapplicable because such modifications are not taught by nor obvious under Nelson, and if incorporated into Nelson, would render Nelson inoperable for its intended functions.

Claims 1-2, 6-7, 10-12, 14, 17, 66 and 69-70 are rejected under 35 U.S.C. §102(e) as being anticipated by Siuzdak et al. (U.S. Patent 6,288,390)

Applicants respectfully traverse these rejections for the reasons presented below.

In order to better understand the differences between Applicants' invention and the '390 (Siuzdak) patent should be recognized that the Applicants' invention is directed to depositing continuous films having optical properties and species adsorption properties essentially the same as the optical properties and the species adsorption properties of the continuous film bulk material that enable the applying a sample to the deposited continuous film. Siuzdak et al. (hereinafter Siuzdak) disclose loading a sample (analyte) onto a porous semiconductor substrate.

As is shown below, a) Siuzdak does not teach depositing a continuous film that has optical properties essentially the same as the optical properties of the continuous film bulk material and b) Siuzdak does not teach the depositing of a continuous film having species

adsorption properties essentially the same as the species adsorption properties of the continuous film bulk material.

a) Siuzdak does not teach depositing a continuous film that has optical properties essentially the same as the optical properties of the continuous film bulk material.

As stated by Siuzdak, "[t]he porosity of the porous silicon can be defined as the amount of silicon lost from the native state of bulk silicon due to anodization and etching." (Siuzdak, col. 11, lines 8-10). To support the Applicant's position, it is pointed out that the pores, as shown in Fig. 1(c) of Siuzdak, are tantamount to particles having a dielectric constant of unity. Thus, porous silicon is tantamount to a composite structure (which can be analyzed by the Bergman theorem or the Clausius-Mosotti equation). The dielectric constant of a composite material is given by a combination of the two dielectric constants. The dielectric constant of the composite (silicon and pores) depends on the combination of the dielectric constant of the silicon bulk material and unity dielectric constant of the pores. The dielectric constant determines several optical properties of interest. Thus, the optical properties of the porous film in Siuzdak are not the optical properties of the continuous film bulk material. For continuous silicon films of the Applicants' invention, the optical properties of the porous silicon in Siuzdak are not essentially the same as the optical properties of the silicon bulk material. (The differences between the optical properties of porous silicon and those of silicon bulk material can be obtained by methods shown in C. Peña, J. Torres, CALCULATION OF OPTICAL CONSTANTS IN POROUS SILICON THIN FILMS USING DIFFUSED AND SPECULAR REFLECTANCE MEASUREMENT, Surface Review and Letters, Vol. 9, Nos. 5 & 6 (2002) 1821-1825.) Therefore, Siuzdak does not teach depositing a continuous film that has optical properties essentially the same as the optical properties of the continuous film bulk material.

b) Siuzdak does not teach the depositing of a continuous film having species adsorption properties essentially the same as the species adsorption properties of the continuous film bulk material.

As stated by Siuzdak, samples containing analyte can be prepared by "*[a]ny method that permits an analyte to reach the pores of the substrate.*" (Siuzdak, col. 16, lines 33-34). Any such method has results including "*physical contact with the substrate, adsorption, and adsorbition.*" (Siuzdak, col. 16, lines 38-39). Thus, the species adsorption properties are related to the porosity and are not essentially the same as the species adsorption properties of the continuous film bulk material. For continuous silicon films of the Applicants' invention, the species adsorption properties of the porous silicon in Siuzdak are not essentially the same as the species adsorption properties of the silicon bulk material. Therefore, Siuzdak does not teach the depositing of a continuous film having species adsorption properties essentially the same as the species adsorption properties of the continuous film bulk material.

As shown above, Siuzdak neither teaches depositing a continuous film having optical properties nor teaches depositing a continuous film having species adsorption properties essentially the same as the optical properties and the species adsorption properties of the continuous film bulk material. The Applicants respectfully assert that amended Claim 1 is not anticipated by the '390 patent (Siuzdak) and neither are any of the dependent claims. In addition, in view of the specific needs of Siuzdak (as discussed above) and since Siuzdak is lacking a patentable feature present in claim 1 and the dependent claims of the Applicants' invention, a modification of Siuzdak under 35 U.S.C. §103 would also be inapplicable because such modifications are not taught by nor obvious under Siuzdak, and if incorporated into Siuzdak, would render Siuzdak inoperable for its intended functions.

Claims 1-2, 6-7, 10-12, 14, 17, 66 and 69-70 are rejected under 35 U.S.C. §103(alas being unpatentable over Siuzdak et al. (U.S. Patent 6,288,390) in view of Mian et al. (6,319,469).

As discussed above, Siuzdak does not disclose depositing a continuous film having optical properties and species adsorption properties essentially the same as the optical properties and the species adsorption properties of the continuous film bulk material. Mian does not disclose depositing a continuous film having optical properties and species adsorption properties essentially the same as the optical properties and the species adsorption properties of the

continuous film bulk material. Therefore combining Siuzdak with Mian cannot be used to establish depositing a continuous film having optical properties and species adsorption properties essentially the same as the optical properties and the species adsorption properties of the continuous film bulk material.

Under a 103 rejection, a prima facie case of obviousness of the invention is made in view of the scope and content of the prior art. In order to establish a *prima facie* case of obviousness, "there must be some suggestion or motivation, either in the references themselves or in the knowledge generally available to one of ordinary skill in the art, to modify the reference or to combine reference teachings. Second, there must be a reasonable expectation of success. Finally, the prior art reference (or references) must teach or suggest all of the claim limitations." MPEP § 2143.

Neither Siuzdak nor Mian separately or in combination teach all the patentable features of amended claim 1. In light thereof, Applicants respectfully traverse the 35 U.S.C. 103 rejection of the claims.

Claims 1 and 15-16 are rejected under 35 U.S.C. §103(a) as being unpatentable over Siuzdak et al. (U.S. Patent 6,288,390) in view of Farmer et al. (J. Mass Spectrom., 1998, 3:697-704).

As stated above, Siuzdak does not disclose depositing a continuous film having optical properties and species adsorption properties essentially the same as the optical properties and the species adsorption properties of the continuous film bulk material. Farmer does not disclose depositing a continuous film having optical properties and species adsorption properties essentially the same as the optical properties and the species adsorption properties of the continuous film bulk material. Therefore combining Siuzdak with Farmer cannot be used to establish not disclose depositing a continuous film having optical properties and species adsorption properties essentially the same as the optical properties and the species adsorption properties of the continuous film bulk material.

Under a 103 rejection, a prima facie case of obviousness of the invention is made in view of the scope and content of the prior art. In order to establish a *prima facie* case of obviousness, "there must be some suggestion or motivation, either in the references themselves or in the

knowledge generally available to one of ordinary skill in the art, to modify the reference or to combine reference teachings. Second, there must be a reasonable expectation of success. Finally, the prior art reference (or references) must teach or suggest all of the claim limitations." MPEP § 2143.

Neither Siuzdak nor Farmer separately or in combination teach all the patentable features of amended claim 1 and the dependent claims. In light thereof, Applicants respectfully traverse the 35 U.S.C. 103 rejection of the claims.

In conclusion, in view of the above remarks, Applicants respectfully request the Examiner find all claims, 1-3, 6-7, 10-12, 14-19, 66-67 and 69-70 as amended and claim 125, allowable over the prior art and pass this case to issue.

Since the total number of claims is less than the number of claims already been paid for, no additional fees are required. However, if fees are required, they should be charged to Deposit Account No. 03-2410, Order No. 30626-101.

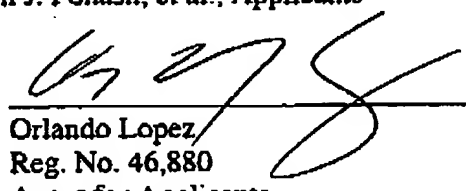
In accordance with Section 714.01 of the MPEP, the following information is presented in the event that a call may be deemed desirable by the Examiner:

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Dated: December 3, 2003

Respectfully submitted,
Stephen J. Fonash, et al., Applicants

By:


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Effective medium theories

Simple effective medium calculations can be done here.

EMC -- the much more complex effective media calculator is created by Volker Ossenkopf.

The "available electromagnetic scattering programs" page is maintained by Thomas Wriedt (Bremen).

The different effective medium theories available on the market have all the same origin, i.e. Maxwell's equations for the static limit. The Bergman theorem (D. Bergman, "The dielectric constant of a composite material - a problem in classical physics", Physics Reports 43, 377-407, [1978]) simply results from this fact. The theorem connects the effective dielectric function of a two-phase composite with the (micro)geometry information about the composite (described by the spectral function $G(L)$) and the dielectric functions of the two components:

$$\epsilon_{eff} = \epsilon_2 \left(1 - f \int_0^1 \frac{G(L)}{t-L} dL \right) \text{ with } t = \frac{\epsilon_2}{\epsilon_2 - \epsilon_1},$$

where f is the volume filling factor of component 1.

In words, the theorem states that

- all possible geometric resonances of a two-phase composite occur for real values of the variable t in the interval $[0,1]$.
- with the integration over L , one scans all possible resonance positions.
- whether a resonance occurs or not is determined by the spectral function $G(L)$ which carries all geometry information.

Therefore, the spectral representation clearly distinguishes between the influence of the geometrical quantities and that of the dielectric properties of the components on the effective behaviour of the system. The spectral representation generally holds as long as the quasistatic approximation is valid. No further restrictions have to be made.

Although the spectral function $G(L)$ is generally unknown for an arbitrary two-phase composite, it's analytically known or can be numerically derived for any existing mixing rule (Stognienko et al. 1995). Because each spectral function has to be non-negative, normalized to unity in the interval $[0,1]$, and obey (for isotropic systems) the first moment equation

$$\int_0^1 L G(L) dL = \frac{1-f}{3},$$

the derivation of $G(L)$ and the check whether these restrictions are fulfilled or not is useful to validate any mixing rule. Note, there are mixing rules in the literature which are not correct with respect to the Bergman spectral representation. E.g. the spectral function for the mixing rule by C.J.F. Böttcher (in: "Theory of Electric Polarization", Elsevier, Amsterdam, p. 415 [1952])

$$\frac{\epsilon_{eff} - \epsilon_2}{3\epsilon_1} = f \frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + 2\epsilon_2} \text{ is } G(L) = 3\delta(L) - 2\delta\left(L - \frac{1}{3}\right)$$

which fulfils only the normalization restriction.

In the following table some mixing rules and their corresponding spectral functions are listed.

Mixing rul	Spectral function
Bruggeman (D.A.G. Bruggeman, "Berechnung verschiedener physikalischer Konstanten von heterogenen Substanzen", Ann. Phys. (Leipzig) 24, 636-679 [1935])	
$f \frac{\epsilon_1 - \epsilon_{\text{eff}}}{\epsilon_1 + 2\epsilon_{\text{eff}}} + (1-f) \frac{\epsilon_2 - \epsilon_{\text{eff}}}{\epsilon_2 + 2\epsilon_{\text{eff}}} = 0$	$\frac{3f-1}{2f} \delta(L) \Theta(3f-1) + \frac{3}{4\pi f L} \sqrt{(L-L^-)(L^+-L)} \Theta(L-L^-) \Theta(L^+-L)$ $\text{with } L^{\pm} = \frac{1}{3} \left(1 + f \pm 2\sqrt{2f-2f^2} \right)$
Maxwell Garnett (J.C.M. Garnett, "Colours in metal glasses and in metallic films", Phil. Trans. R. Soc. Lond. 203, 385-420 [1904])	
$\frac{\epsilon_{\text{eff}} - \epsilon_2}{\epsilon_{\text{eff}} + 2\epsilon_2} = f \frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + 2\epsilon_2}$	$\delta\left(L - \frac{1-f}{3}\right)$
Looyenga (H. Looyenga, "Dielectric constants of heterogeneous mixtures", Physica 31, 401-406 [1965])	
$\epsilon_{\text{eff}}^{1/3} = f\epsilon_1^{1/3} + (1-f)\epsilon_2^{1/3}$	$f^2 \delta(L) + \frac{3\sqrt{3}}{2\pi} \left[(1-f) \left \frac{L-1}{L} \right ^{1/3} + (1-f)f \left \frac{L-1}{L} \right ^{2/3} \right]$
PCA/CCA aggregate equivalent (Stognienko et al. 1995, Henning and Stognienko 1996)	
$\epsilon_{\text{eff}} = \epsilon_2 \left(1 - \frac{fg_0}{t} - \frac{fg_1}{t-L_1} \right)$	$g_0 \delta(L) + g_1 \delta(L-L_1)$
$g_1 = 1 - g_0, L_1 = \frac{(1-f)}{3g_1}, \text{ with percolation strength}$	
$g_0 = \frac{2+f}{3} \left(1 - \frac{2}{1 + \exp(40(f-f_0))} \right), \quad \begin{matrix} f_0^{\text{PCA}} = 0.04 \\ f_0^{\text{CCA}} = 0.0 \end{matrix}$	
Monecke (J. Monecke, "Bergman spectral representation of a simple expression for the dielectric response of a symmetric two-component composite", J. Phys.: Cond. Mat. 6, 907-912 [1994])	

$$\epsilon_{\text{eff}} = \frac{2(f\epsilon_1 + (1-f)\epsilon_2)^2 + \epsilon_1\epsilon_2}{(1+f)\epsilon_1 + (2-f)\epsilon_2} \quad \frac{2f}{1+f} \delta(L) + \frac{1-f}{1+f} \delta\left(L - \frac{1+f}{3}\right)$$

Hollow sphere equivalent

(see, e.g., C.F. Bohren and D.R. Huffman "Absorption and Scattering of Light by Small Particles", Wiley, New York, p. 149 [1983])

$$\epsilon_{\text{eff}} = \epsilon_1 \frac{(3-2f)\epsilon_2 + 2f\epsilon_1}{f\epsilon_2 + (3-f)\epsilon_1} \quad \frac{2}{3-f} \delta(L) + \frac{1-f}{3-f} \delta\left(L - \frac{3-f}{3}\right)$$

$$f = 1 - \frac{r_i^3}{r_o^3}, \quad r_{i/o} = \text{inner/outer radius of the sphere}$$

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R. Stognienko, Feb 1997

CALCULATION OF OPTICAL CONSTANTS IN POROUS SILICON THIN FILMS USING DIFFUSED AND SPECULAR REFLECTANCE MEASUREMENT

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In this work a method is proposed to calculate the optical constants of porous silicon (PS) thin films. The method is based on the theoretical simulation of the experimental reflectance spectra. In the optical system of this method the PS is considered a homogeneous, absorbing thin film, deposited on a silicon substrate of semi-infinite dimension. The theoretical form of the systems reflectance is calculated using the summation method proposed by Airy. Light scattering is included in the model by introducing the Davies-Bennett relation. The refraction index of the material is fit with the simple harmonic oscillator, proposed by Weemple-DiDomenico. The model was tested on two samples fabricated with anodization times of 25 and 35 min, the values for the refraction indexes, absorption coefficients, thickness and roughness were calculated for both samples. The PS samples were fabricated by electrochemical anodization of single crystal p-type silicon substrates in HF (25%) + isopropyl alcohol solution.

1. Introduction

After Canham's report on an intense photoluminescence signal in porous silicon (PS),¹ a great deal of work has been carried out, attempting to explain the optical behavior of this material. The optical response of the PS to the visible suggests the possibility of using it as an active optical element in circuits with silicon technology, bypassing the optical limitation of silicon in this spectral region. To obtain the optical constants of PS it is preferable to use reflectance or ellipsometry measurements, since they are nondestructive techniques applicable to films deposited on opaque substrates.² Independently of the type of measurements, the optical constants are obtained through the theoretical reproduction of the

experimental spectra. However, this simulation is hard to carry out on PS given the great variety of inhomogeneities present in this material; these inhomogeneities cause an important amount of scattering of light, which then demands the inclusion of this fact in the model to obtain a better simulation of the experimental reflectance spectra. In this context, the precision on the optical constants depends upon the proximity of the simulated with the experimental spectrum. There is proposed in this work a simple calculation method to obtain the optical properties: index of refraction $n_2(\lambda)$, absorption coefficient $\alpha(\lambda)$, thickness and roughness of the PS film. The method is based on the theoretical reproduction of experimental reflectance spectra taken between 300 and

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1000 nm. The model is tested on several films of porous p-type silicon fabricated at different anodization times.

2. Theory

During the anodization process small perforations (pores) are made in the silicon surface, such that the PS film is made up of two phases: air filling up the pores and solid silicon constituting the pore walls. This disorderly two-phase system can be treated as an effective medium, given that the dimensions of the solid phase in the film is small in comparison with the electromagnetic wavelength.³ We consider, in our model, the porous material as homogeneous and assign to it an effective index of refraction. To reproduce, under these conditions, the experimental spectra, we must calculate the reflectance of a film consisting of a homogeneous material thin film deposited on a single-crystal silicon substrate of semi-infinite thickness.⁴ (See Fig 1)

The reflectance is calculated, in this new system, from the summation theory of the light beams reflected and transmitted at the air/PS, PS/silicon interfaces proposed by Fresnel.⁵ The sum takes into account the absorption by both the homogeneous material and the substrate, which are included in the model using Lambert's relation. Finally, the Davies-Bennett relation⁶ is used to include light scattering produced by the sample. The expression obtained, in this case, for the reflectance is

$$R_s = R e^{-\frac{2\pi\sigma d}{\lambda}}, \quad (1)$$

where

$$R = \frac{r_{12}^2 + 2r_{12}r_{23} \cos 2\delta + r_{23}^2}{1 + 2r_{12}r_{23} \cos 2\delta + r_{12}^2 r_{23}^2}, \quad (2)$$

$$r_{12} = \frac{\eta_1 - \eta_2}{\eta_1 + \eta_2}, \quad (3)$$

$$r_{23} = \frac{\eta_2 - \eta_3}{\eta_2 + \eta_3} \quad (4)$$

$$\delta = \frac{4\pi\eta_2 d}{\lambda}. \quad (5)$$

R is the totally reflected (specular and scattering) intensity assuming an ideal sample with parallel and flat interfaces, $\eta_1 = 1$ is the air's index of refraction, $\eta_2 = n_2 - ik_2$ is the effective index associated to the PS film, $\eta_3 = n_3 - ik_3$ is the index of refraction

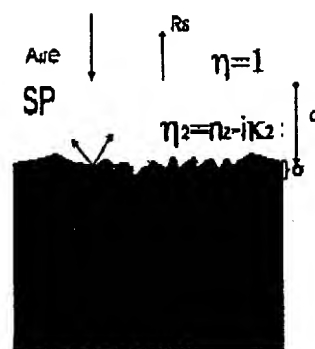


Fig 1 The porous silicon is considered a homogeneous material to which is associated an effective index of refraction. The homogeneous film is deposited on a semi-infinite substrate.

for the substrate, considered in this work as single-crystal silicon.⁷ σ is the roughness of the material, d the thickness of the PS film and λ the wavelength; r_{12} and r_{23} are the Fresnel coefficients for the air/PS, PS/silicon interfaces.

3. Results

3.1. Calculation procedure

Initially n_2 , thickness and absorption coefficient are calculated using the experimental spectrum for the total reflectance $R_{exp} = R_{s,exp} + D$, where $R_{s,exp}$ is the total experimental reflectance, $R_{s,exp}$ the specular reflectance of the PS sample and D the scattering spectrum. We considered in this spectrum two calculation regions: a high absorption region where the interference fringes disappear and a transparent one ($k_2, k_3 \sim 0$), arbitrarily assigned to the region where the interference fringes appear. The goal in this first part of the calculation is to obtain a value for the thickness of the sample, which is achieved through the following procedure:

- (1) The order of interference (m) associated to each minimum and maximum is determined using the relation

$$m \approx \frac{\lambda_{m-1}}{\lambda_{m-1} - \lambda_m}. \quad (6)$$

- (2) A rough value for n_2 is calculated at the minima using the relation

$$R = \left(\frac{n_2^2 - n_1 n_3}{n_2^2 + n_1 n_3} \right)^2. \quad (7)$$

The values for n_2 obtained in such a way are interpolated using a line between the two wavelengths associated to each maximum of the spectrum. With these values for the index of refraction, plus the relation $\delta = m\pi$ [Eq. (5)], approximate values for the PS film thickness are obtained. Next we improve the refraction indexes obtained in the previous procedure.

- (3) A more real value for n_2 is determined in all the spectrum with the thickness average value, this is done comparing permanently the experimental spectrum with the theoretical in each wavelength, using the relation

$$R(n_1(\lambda), n_2(\lambda), k_3(\lambda), d, n_2(\lambda)) - R_{exp} \approx 0. \quad (8)$$

This procedure must be carried out for each wavelength of the spectrum, which might make the calculation highly time-consuming; to reduce the calculation time, the index of refraction is fit with the single-effective-oscillator model proposed by Wemple-DiDomenico⁸: $n_2^2 = 1 + \frac{E_0 E_d}{E_0^2 - (\hbar\omega)^2}$, where $\hbar\omega$ is the photon energy, E_0 the single oscillator energy and E_d the dispersion energy. The inclusion of this relation in Eq. (8) makes it n_2 -independent, but now E_0 and E_d must be calculated here.

- (4) Once we have obtained the values for the index of refraction in the measured spectral region and the thickness of the sample, it is time to calculate the absorption coefficient, in all of the spectrum, using again Eq. (9). In this case, the absorption coefficient is included in it as $\alpha_2 = \frac{4\pi k_2}{\lambda}$, k_2 being the extinction coefficient.

$$R(n_1(\lambda), n_2(\lambda), k_3(\lambda), d, n_2(\lambda), k_2(\lambda)) - R_{exp} \approx 0. \quad (9)$$

- (5) Finally, the roughness is calculated using the relation $R_{exp} = R_{exp} - D$, where D is the scattering spectrum measured in the sample

$$R(n_1(\lambda), n_2(\lambda), k_3(\lambda), d, n_2(\lambda), k_2(\lambda), \sigma) - R_{exp} \approx 0 \quad (10)$$

3.2. Fabrication and characterization of the samples

The PS thin films were fabricated by electrochemical anodization of silicon substrates in HF(25%) +

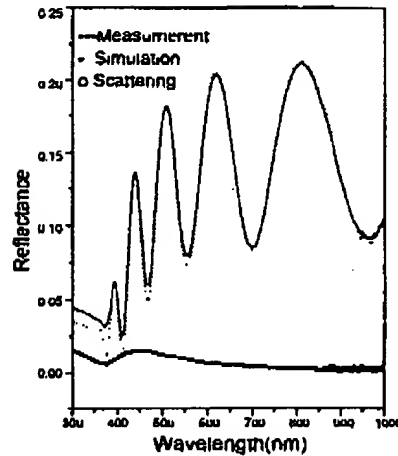


Fig. 2 Experimental total reflectance spectrum compared to the simulated one for the 25 min anodization sample.

isopropyl alcohol solution. Type p, (100), resistivity from 0.7 to 1 Ω cm single-crystal silicon substrates were used. The anodization current was 11 mA. Here, we present results of two samples fabricated with anodization times of 25 and 35 min. The reflectance spectra were obtained with normal-incidence light beam on the sample surface, using a Perkin Elmer lambda 900 spectrophotometer, with integrating sphere. The diffuse light spectra were obtained also with normal-incidence light, with the integrating sphere placed in such way as to discount the specular reflectance of the sample.

3.3. Discussion

In Figs. 2 and 3 are shown the R_{exp} and D spectra, measured for the 25 and 35 min samples, together with the simulated one. As can be seen in the figures, the simulation reproduces acceptably the experimental spectra, except at the high-energy region; in this region the index of refraction and absorption coefficient cannot be calculated independently one of the other, which makes its fitting very difficult. It is also possible that, in this region, the proposed harmonic oscillator model would not be feasible. Figures 4 and 5 show, respectively, the values for index of refraction and absorption coefficient obtained with the model, for both samples. Although the indexes, obtained for PS, present lower values than for single-crystal

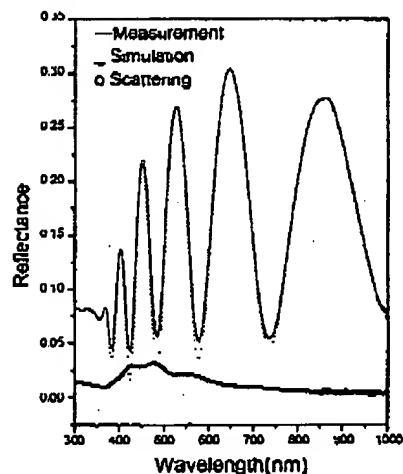


Fig. 3. Experimental total reflectance spectrum compared to the simulated one for the 35 min anodization sample

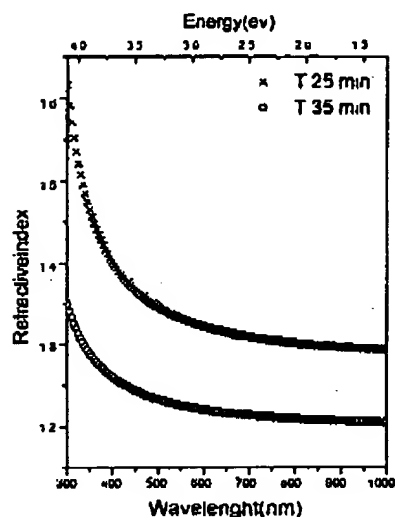


Fig. 4. Effective indexes of refraction obtained for both 25 and 35 min anodization time samples.

silicon, these values must be subject to a new calculation procedure, a mixing rule like Maxwell-Garnets or Bruggeman,⁹ to determine the form in which the two phases mix. It is also observed that the index of refraction values obtained for the 35 min sample are lower than for the 25 min one. This can be explained considering that the longer the anodization time, the

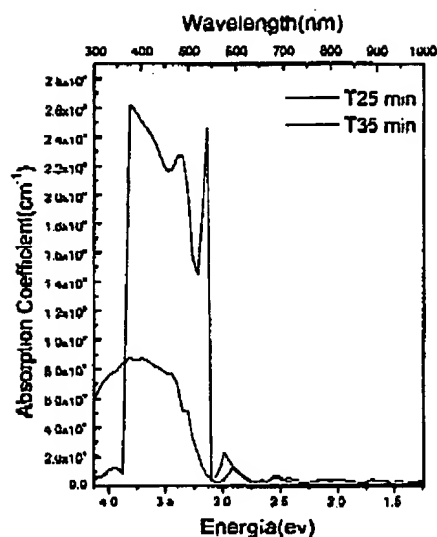


Fig. 5. Calculated absorption coefficients obtained for both samples

Table 1. Parameters obtained through simulation: σ is the roughness of the sample, d the calculated thickness and d_p the thickness measured using the alpha-step technique; E_d and E_0 are parameters obtained for the single-effective-oscillator.

Sample	E_d (eV)	E_0 (eV)	σ (nm)	d (μm)	d_p (μm)
25 min	3.4	5.32	7.5	0.93	1.24
35 min	2.6	6.00	8.7	1.06	1.49

greater the removal of the solid phase from the sample, which might increase the amount of air in the film. The absorption curves present structure and it is important to mention that other authors, following different calculation procedures, have reported similar curves¹⁰, other papers show that this type of absorption might be related with absorption of light by quantum threads.¹¹ Table 1 shows the calculated parameters for each sample and compares the theoretically obtained thickness with the experimental one, using the alpha-step technique.

4. Conclusions

A simple procedure was proposed to determine the optical constants of PS thin films, from the theoretical simulation of reflectance spectra. The spectral values for the index of refraction, the absorption

coefficient and the thickness of the sample are obtained using in the calculation the total reflectance spectrum, while the roughness of the sample was calculated using the $R_{exp} = R_{exp} - D$ spectrum, where D is the diffuse light spectrum reflected by it. The reliability of the method was tested by reproducing several spectra using calculated parameters. The comparison of the experimental and simulated spectra is satisfactory in the visible and near infrared region. The deficiency in the ultraviolet region is possibly due to the great difficulty of extrapolating the index of refraction to this region where a high absorption predominates and the ruggedness has a strong influence. It was observed that the index of refraction, the absorption coefficient and the thickness of the sample strongly depend on the anodization time. The method can also be applicable on other thin films grown on thick substrates presenting interference patterns.

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